DRL No. 93/DRD No. MF-3

DOE/JPL - 955318 - 79/1

DISTRIBUTION CATEGORY UC-63

A NEW METHOD OF METALLIZATION FOR SILICON SOLAR CELLS.

FIRST QUARTERLY REPORT

FOR PERIOD COVERING

15 DECEMBER 1978 TO 31 MARCH 1979

BY

DR. MILO MACHA

JPL CONTRACT NO. 955318

SOL/LOS INCORPORATED
2231 S. CARMELINA AVENUE
LOS ANGELES, CA. 90064

" THE JPL LOW-COST SILICON SOLAR ARRAY PROJECT IS SPONSORED BY THE UNITED STATES DEPARTMENT OF ENERGY AND FORMS PART OF THE SOLAR PHOTOVOLTAIC CONVERSION PROGRAM TO INITIATE A MAJOR EFFECT TOWARD THE DEVELOPMENT OF LOW-COST SOLAR ARRAYS. THIS WORK WAS PERFORMED FOR THE JET PROPULSION LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY BY AGREEMENT BETWEEN NASA AND DOE. "

DRL No. 93/DRD No. MF-3

DOE/JPL - 955318 - 79/1

Distribution Category UC-63

A NEW METHOD OF METALLIZATION FOR SILICON SOLAR CELLS.

FIRST QUARTERLY REPORT

FOR PERIOD COVERING

15 DECEMBER 1978 TO 31 MARCH 1979

BY

DR. MILO MACHA

JPL CONTRACT NO. 955318

SOL/LOS INCORPORATED
2231 S. CARMELINA AVENUE
LOS ANGELES, CA. 90064

" The JPL Low-Cost Silicon Solar Array Project is sponsored by the United States Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effect toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE. "

ABSTRACT

THE OBJECTIVE OF THIS PROGRAM IS TO DEVELOP A LOW-COST OHMIC CONTACT ON SILICON SOLAR CELLS BASED ON MOLYBDENUM TIN METAL SYSTEM.

THE APPROACH IS BASED ON THE FORMULATION OF A SCREENABLE INK COMPOSED FROM MOLYBDENUM OXIDE AND TIN MIXTURE.

THE FIRST QUARTER OF THIS PROGRAM INVOLVED THE STUDY OF THE REDUCTION OF MoO_3 INTO Mo AND THE ESTABLISHING OF MoO_3:Sn RATIO.

BOTH TASKS HAVE BEEN DONE IN AN EXPERIMENTAL STATION CONSTRUCTED FOR THIS PURPOSE. THE RESULTS SHOWED THAT MOLYBDENUM WAS FORMED FROM ITS OXIDE AT $800^{\circ}C$ AND IMPROVED IN BONDING TO SILICON AT $900^{\circ}C$.
A 20% MoO_3-80% Sn MIXTURE WAS CONVERTED INTO A METALLIC COATING WITHIN THIS TEMPERATURE RANGE.

THE NEXT QUARTER WILL BE CONCERNED WITH THE FORMULATION OF SCREENABLE INK, CALIBRATION OF A TUBE FURNACE FOR THE FIRING CYCLE AND EVALUATION OF THE METAL CONTACT ON SOLAR CELL STRUCTURES.

TABLE OF CONTENTS

I. INTRODUCTION

METALS FOR OHMIC CONTACT TO SILICON SOLAR CELLS ARE SELECTED ON BASIS OF THEIR ELECTRICAL CONDUCTIVITY, THERMAL EXPANSION COEFFICIENT, ENVIRONMENTAL STABILITY AND COST.

TABLE I SHOWS THE PERTINENT PROPERTIES OF METALS. THIS TABLE SHOWS THAT MOLYBDENUM IS MOST DESIRABLE WITH RESPECT TO THE STATED REQUIREMENTS. IT HAS THE CLOSEST MATCH OF THERMAL EXPANSION COEFFICIENT WITH SILICON FROM ALL METALS AND IT IS AMONG TEN OF THE HIGHEST CONDUCTIVE METALS, ONLY SECOND TO COPPER AMONG THE COMMON METALS. FOR THIS REASON MOLYBDENUM IS USED IN SILICON DEVICE TECHNOLOGY AS A STRUCTURAL ELEMENT IN THE DEVICE AND CIRCUIT ASSEMBLY. IT IS USED AS A MECHANICAL SUPPORT AS WELL AS A HEAT SINK. AS A CONTACTING ELEMENT HOWEVER MOLYBDENUM IS USED VERY RARELY AND THE REASON FOR THIS IS THAT ITS HIGH MELTING AND BOILING POINT MAKE THE DEPOSITION OF THE FILM BY EVAPORATION OR SPUTTERING RATHER DIFFICULT AND FILM FORMATION BY PYROLYTIC DECOMPOSITION OF CARBONYLS OR HALIDE COMPOUNDS REQUIRES COMPLEX EQUIPMENT AND PROCESSING STEPS.

THE FORMATION OF MOLYBDENUM FILMS BY A SIMPLE AND ECONOMIC PROCESS IS THE SUBJECT OF THIS PROGRAM. IT IS BASED ON THE CONVERSION OF MOLYBDENUM TRIOXIDE (MoO_3) INTO METALLIC MOLYBDENUM IN A REDUCING ATMOSPHERE AT

TABLE I

PROPERTIES OF METALS

	ELECTRICAL RESISTIVITY (OHMS-CM)	COEF. OF THERMAL EXPANSION (CM/CM/°C).10^{-6}	MELT. P. (°C)	BOIL. P. (°C)	DENSITY (G/CM^2)
TITANIUM	176	7.1	$1725^{+}10$		4.5
NICKEL	65.3	9.2	1455	3075	8.9
LEAD	20.6	16.3	327	1740	11.3
PLATINUM	14.9	4.9	1774	4530	21.5
TANTALUM	12.4	4.0	2996	4100	16.6
TIN	11.5	13	232	2260	7.3
PALLADIUM	10.8	6.5	1555	3980	12.0
ALUMINUM	6.3	13.7	660	1800	2.82
ZINC	6.1	19.3	419	904	7.17
TUNGSTEN	5.48	2.2	3410	5900	19.4
MOLYBDENUM	5.17	3.1	2622	4570	10.2
BERYLLIUM	5	6.4	$1292^{+}8$	2980	1.84
RHODIUM	4.51	4.6	1966		12.4
GOLD	2.35	7.9	1065	2700	19.3
COPPER	2.03	9.8	1083	2595	8.95
SILVER	1.6	10.9	960	2000	10.5
SILICON		4.2	1420		2.33

ELEVATED TEMPERATURES. MOLYBDENUM TRIOXIDE (MoO_3) IS THE MOST STABLE OXIDATION STATE OF MOLYBDENUM AND HAS AN ADVANTAGEOUS CHARACTERISTIC IN THAT IT HAS A RELATIVELY LOW MELTING POINT OF $795^{o}C$ AND IS ALSO EASILY TO REDUCE INTO MOLYBDENUM METAL. WHEN HEATED IN AIR IT STARTS TO SUBLIME ABOVE $550^{o}C$, MELTS INTO AN OILY LIQUID AT $795^{o}C$, AT WHICH POINT THE SUBLIMATION IS EXCEEDINGLY HEAVY. IN REDUCING ATMOSPHERE, ON THE OTHER HAND, THIS OXIDE REDUCES AT APPROXIMATELY $600^{o}C$ INTO LOWER OXIDES, MOSTLY MoO_2, WHICH IS CHARACTERIZED BY A PURPLE COLOR. MoO_2 DOES NOT SUBLIME AND CAN BE ULTIMATELY REDUCED TO MOLYBDENUM METAL ABOVE $600^{o}C$, IF KEPT FOR A LONG ENOUGH TIME. WHEN THE TEMPERATURE IS INCREASED TO $796^{o}C$ OR ABOVE, THE RESIDUAL MoO_3 STILL PRESENT IN THE OXIDE MIXTURE MELTS AND IS CONVERTED INTO A DENSE MOLYBDENUM FILM.

SINCE THE MoO_3 IS COMMONLY AVAILABLE IN A FINE POWDER FORM, IT IS VERY SUITABLE TO USE IN A SUSPENSION ADJUSTED FOR SILK SCREENING PROCESSES.

THE SECOND ELEMENT IN THE PROPOSED METALLIZATION METHOD IS TIN. IT IS SELECTED BECAUSE OF ITS GOOD SOLDERABILITY AT LOW TEMPERATURES AND ALSO BECAUSE IT HAS THE HIGHEST ELECTRICAL CONDUCTIVITY AMONG THE LOW MELTING METALS.

NO CONCLUSIVE INFORMATION IS AVAILABLE ON THE CONSTITUTION OF MOLYBDENUM-TIN SYSTEM.

THERE ARE REFERENCES STATING THAT UPTO 0.13% TIN IN MOLYBDENUM FORMS A SINGLE PHASE. THIS REFERENCE CAN BE FOUND IN THE CONSTITUTION OF BINARY ALLOYS BY F.A.SHUNK, 1969 (SECOND EDITION).

THERE IS EXPERIMENTAL EVIDENCE THAT MOLYBDENUM IS READILY WET BY TIN IN THE ABSENCE OF OXIDE AND THIS REACTION IS MORE PRONOUNCED WHEN IT TAKES PLACE AT THE TIME WHEN MOLYBDENUM IS REDUCED FROM ITS OXIDE. THEREFORE THE AIM IS TO FORMULATE A MOLYBDENUM OXIDE-TIN COMPOSITION, DISPERSE IT IN A SUITABLE VEHICLE FOR SILK SCREENING AND FORM THE CONTACT ON THE SOLAR CELL SURFACE BY FIRING THIS MIXTURE IN REDUCING ATMOSPHERE.
FORMING GAS IS USED FOR SAFETY REASONS.

THE PROJECT IS PLANNED IN THREE PHASES.

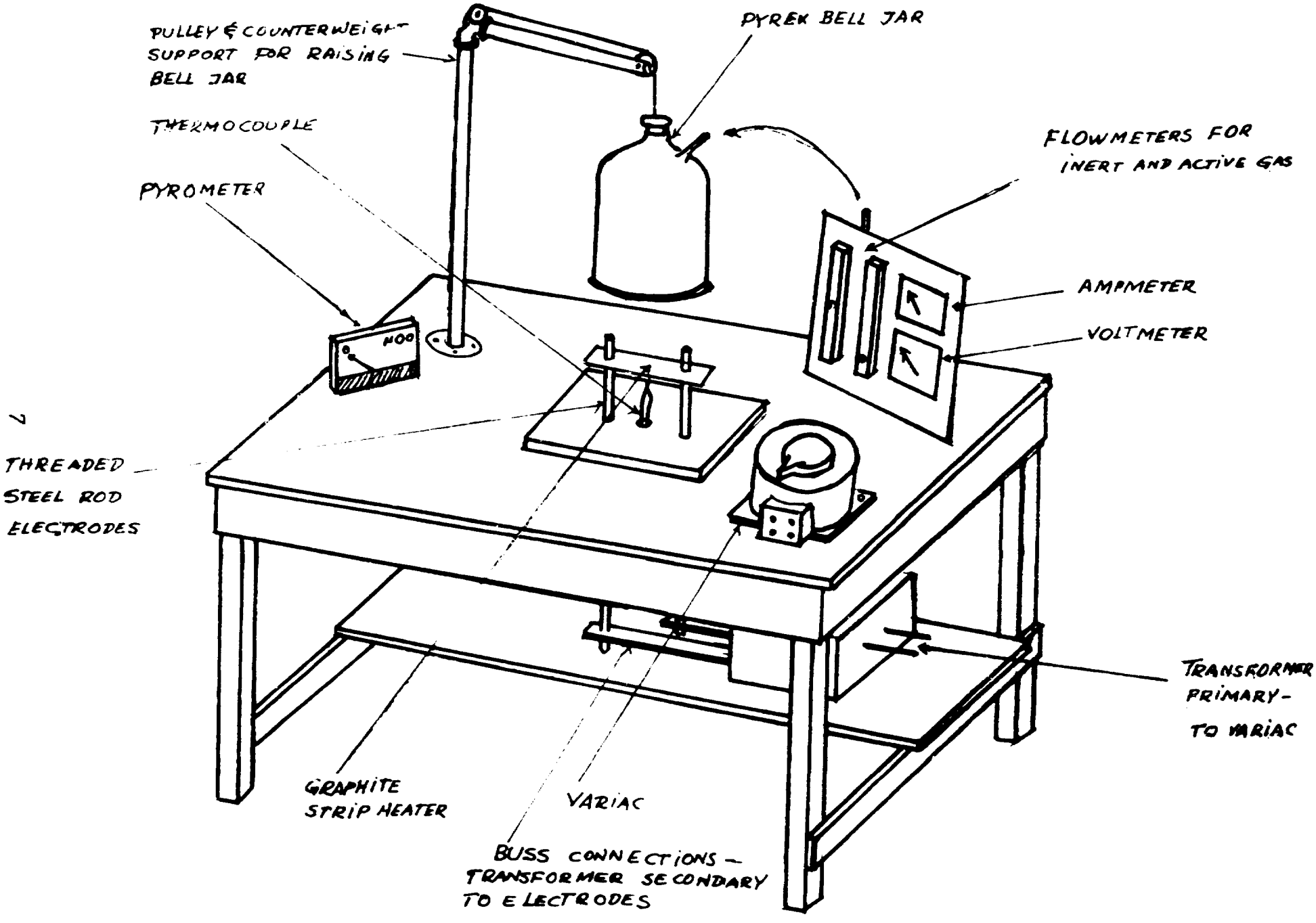
1. THE DETERMINATION OF THE CYCLE FOR CONVERSION OF MoO_3 INTO Mo AND THE RATIO OF MoO_3:Sn.
   THIS PHASE IS DONE IN AN EXPERIMENTAL STATION, ESPECIALLY CONSTRUCTED FOR THIS PURPOSE.
2. THE FORMULATION OF SCREENABLE INK AND THE EVALUATION OF THE CONTACT ON SOLAR CELLS. THIS WORK IS CONDUCTED IN A TUBE FURNACE CALIBRATED TO PARAMETERS ESTABLISHED EXPERIMENTALLY IN THE FIRST PHASE.
3. THE SPECIFICATION OF THE PROCESS FOR METALLIZATION IN CONVEYOR BELT FURNACES.

II. ACCOMPLISHMENTS

THE FIRST QUARTER OF THE PROGRAM WAS CONCERNED WITH ESTABLISHING OF THE TEMPERATURE-TIME-ATMOSPHERE CYCLE REQUIRED FOR THE REDUCTION OF MOLYBDENUM TRIOXIDE INTO MOLYBDENUM AND ALSO DETERMINATION OF MOLYBDENUM TRIOXIDE-TIN RATIO TO OBTAIN SOLDERABLE AND ADHERENT COATINGS.

II. 1. CONSTRUCTION OF EXPERIMENTAL STATION.

THE PURPOSE OF THIS STATION IS TO ALLOW FOR VISUAL OBSERVATION OF REACTIONS TAKING PLACE UNDER VARIOUS TEMPERATURE-TIME-ATMOSPHERE HEATING CYCLES AND TO PERFORM INDIVIDUAL EXPERIMENTS IN A SHORT TIME. THE STATION SHOWN IN THE ATTACHED SKETCH CONSISTS OF A GRAPHITE STRIP HEATER, LOCATED UNDER A PYREX BELLJAR WITH AN INLET FOR GASFLOW. THE GRAPHITE STRIP IS HEATED BY MEANS OF AC CURRENT AND DESIGNED TO GENERATE 1000°C. THE TEMPERATURE OF THE STRIP IS MONITORED BY A CHROMEL-ALUMEL THERMOCOUPLE AND DISPLAYED BY A PYROMETER. THE ATMOSPHERE IN THE BELLJAR IS CONTROLLED BY FLOWMETERS AND VALVES TO PROVIDE A DESIRABLE INERT OR REACTIVE GASEOUS ENVIRONMENT.
THE HEATER IS CONSTRUCTED FROM A HIGH PURITY POCO GRAPHITE DISTRIBUTED BY: GRAPHITE MACHINED PRODUCTS
9806 EVEREST STREET
DOWNEY, CALIF. 90242

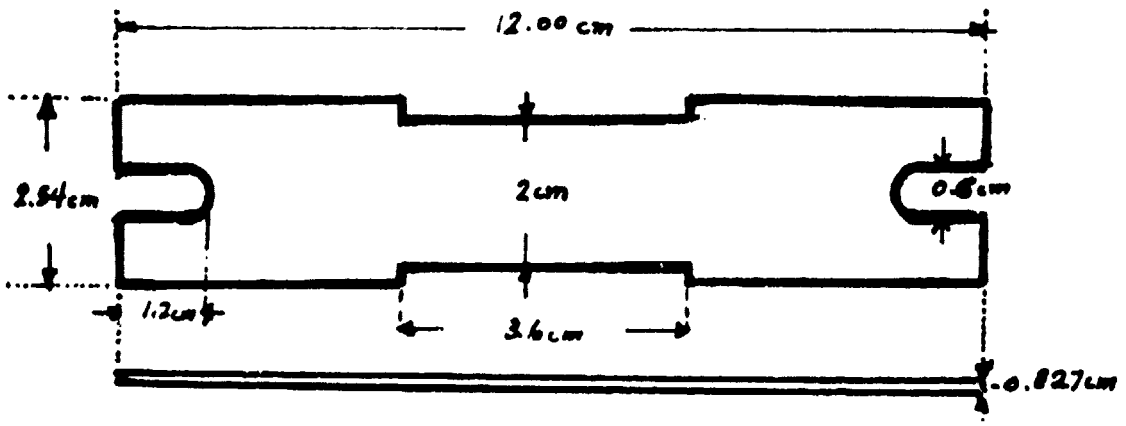


CONTROLLED ATMOSPHERE EXPERIMENTAL STRIP HEATER

THE DENSITY OF THIS MATERIAL IS 1.84G/CM^3 AND RESISTIVITY $1.27 \times 10^{-3}\Omega$-CM.

THE SUPPLIED MATERIAL IS 4"(10.16CM) WIDE, 6"(15.24CM) LONG AND .050"(0.127CM) THICK.

THE HEATING ELEMENT IS SHAPED FROM THIS PLATE AND HAS DIMENSIONS OF 1"(2.54CM) X 4.72"(12CM) WITH SLOTS ON EACH NARROW END FOR MOUNTING TO THE ELECTRODES TERMINALS (SEE DRAWING).



THE ELECTRICAL ENERGY FOR THE HEATER IS SUPPLIED BY 120VOLTS-20AMPS IN-HOUSE LINE VIA THREE TRANSFORMERS EACH ONE HAVING 208 VOLTS-10.8AMPS RATING ON THE PRIMARY AND 30VOLTS-60AMPS ON THE SECONDARY WINDING.

THE PRIMARIES OF THESE TRANSFORMERS ARE CONNECTED IN SERIES, THE SECONDARIES IN PARALLEL. THE VOLTAGE TO THE PRIMARY IS REGULATED BY A VARIAC.

AS A SINGLE TRANSFORMER OF PROPER RATING WAS NOT READILY AVAILABLE, WE USED THE THREE TRANSFORMERS IN THE ABOVE DESCRIBED ARRANGEMENT.

The temperature of the strip is monitored by a Chromel-Alumel thermocouple, gauge 28, purchased from California Alloy Co., El Monte, Calif. and recorded on a pyrometer with a scale from 0 - 1100°C, purchased from the same company. The external resistance of the thermocouple is adjusted to 10 Ohms in order to match the resistance of the pyrometer.

The belljar is from pyrex glass, has the diameter of 8"(20.32 cm) and has a volume of 12 liters.
It is suspended by a wire cord and balanced by a counter weight.
The flowmeters to control the gas flow are made by Brooks Instrument Division Emerson Electric Co., Hatfield, Penn. One, used for forming gas, has a maximum flow-rate of 4.7 std.l/min and the minimum flow-rate of 0.1 std l/min. The other, used for nitrogen, has the maximum flow-rate of .272 std l/min and a minimum rate of .014 std l/min.

II. 2. Reduction of MoO_3 into Mo.

Materials used:

Silicon wafers P-type, 1 Ohm-cm and
N-type, 0.1 Ohm-cm

Molybdenum oxide reagent (Mallinckrodt)

Trichloro ethylene

Ethylcellulose (Dow Chemical Co.)

The silicon wafers were scribed to 1x1 cm approx., etched cleaned in 9:1 = HNO_3:HF

THE MOLYBDENUM OXIDE SUSPENSION WAS PREPARED BY DISPERSING MoO_3 IN TRICHLORO ETHYLENE AND A SMALL AMOUNT OF ETHYLCELLULOSE WAS ADDED TO ADJUST TO A CONSISTENCY OF A PAINT.

NO EXACT RATIO OF INDIVIDUAL INGREDIENTS WAS ESTABLISHED AS THE PURPOSE OF THESE TESTS WAS TO DETERMINE QUALITATIVELY THE REDUCTION OF MoO_3.

THE SILICON WAFERS WERE COATED ON ONE SIDE WITH THIS SUSPENSION.

THE SAMPLES WERE SUBJECTED TO A HEAT CYCLE TO FORM Mo.

THE Mo COATINGS WERE EVALUATED FOR LATERAL CONDUCTANCE AND BOND STRENGTH. THE CONDUCTANCE WAS MEASURED BY AN OHM METER AND THE BOND STRENGTH BY A SCRATCH TEST USING AN X-ACTO KNIFE.

THE FIRST CYCLE HAD A PEAK TEMPERATURE OF $800^{o}C$ AND THE HEAT-UP WAS DONE IN STEPS TO OBSERVE MATERIAL CHANGES AT DIFFERENT TEMPERATURES.

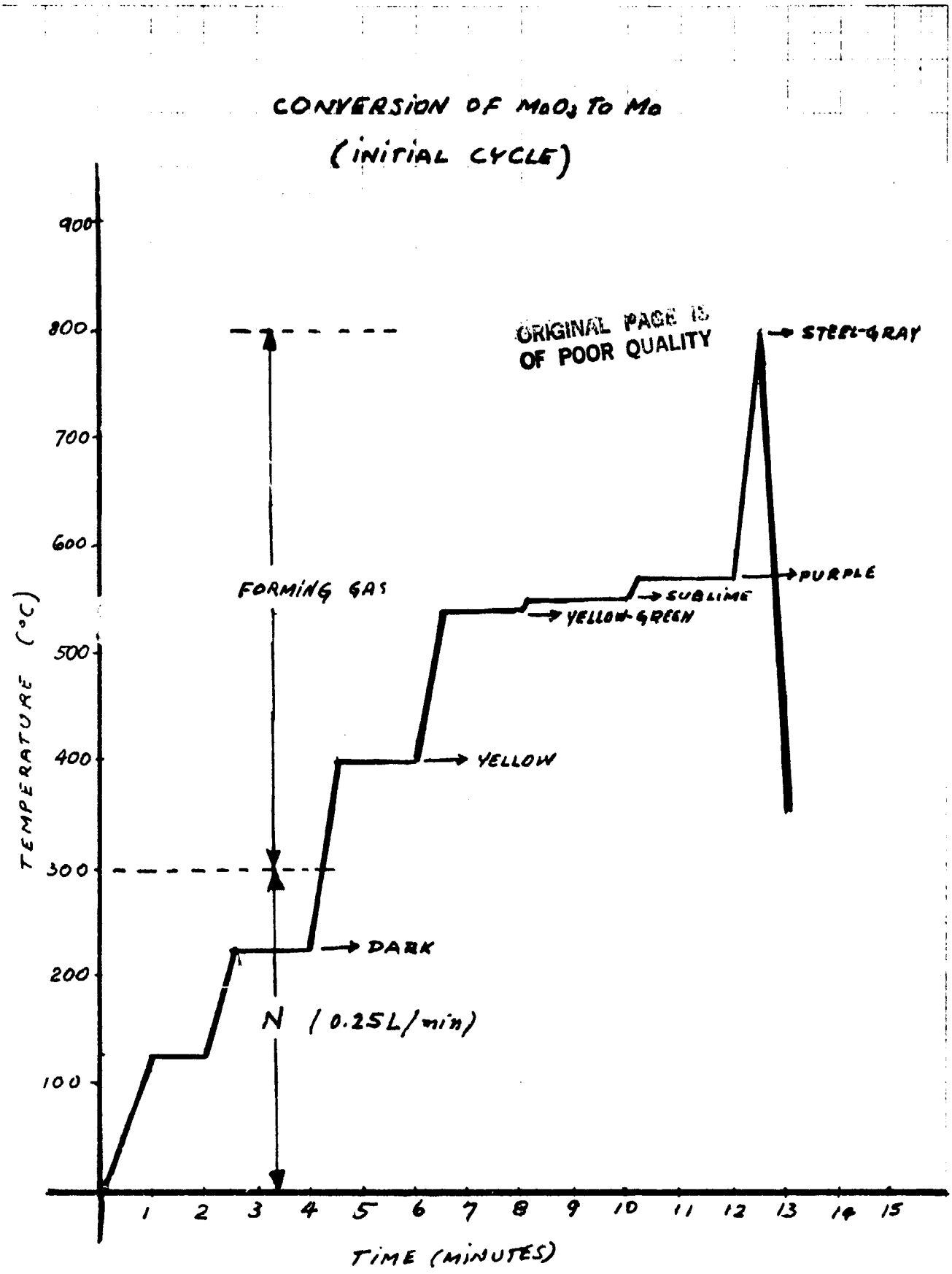
THE GRAPH SHOWS THIS CYCLE.

THE INITIAL HEATING WAS DONE IN NITROGEN FLOW OF .25L/MIN AND AT $225^{o}C$ THE DARK COLOR APPEARED, CORRESPONDING TO THE CARBONIZATION OF THE ORGANIC BINDER IN THE COATING.

THE FORMING GAS WAS TURNED ON AT $300^{o}C$ WITH A FLOW-RATE OF 2.5 L/MIN.

AT $400^{o}C$ YELLOW COLOR OF THE ORIGINAL MoO_3 REAPPEARED.

AT $540^{o}C$ THE COLOR BECAME GREENISH AND AT $550^{o}C$ SOME SUBLIMATION WAS OBSERVED.


CONVERSION OF MoO3 TO Mo
(INITIAL CYCLE)
ORIGINAL PAGE IS
OF POOR QUALITY
900
800
700
600
500
400
300
200
100
TEMPERATURE (°C)
FORMING GAS
STEEL-GRAY
PURPLE
SUBLIME
YELLOW-GREEN
YELLOW
DARK
N (0.25L/min)
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
TIME (MINUTES)

At 570°C the color turned dark purple and this persisted till the peak of 800°C, at which point the color changed to steel-gray. The temperature was quenched suddenly to room temperature.

The films had a resistance between 5-10 Ohms and a reasonable good bond to silicon, P-type as well as N-type, yet it was possible to be scraped off by a X-acto knife.

The forming gas used for the reduction was composed of 85% nitrogen and 15% hydrogen.

Experiments were done also with 60% nitrogen and 40% hydrogen.

The results in both cases were identical except with the higher hydrogen content the reduction of the oxide was faster.

The conclusion drawn from these experiments was that the transition temperature from 550°C to 650°C was critical with respect to the sublimation and loss of MoO_3.

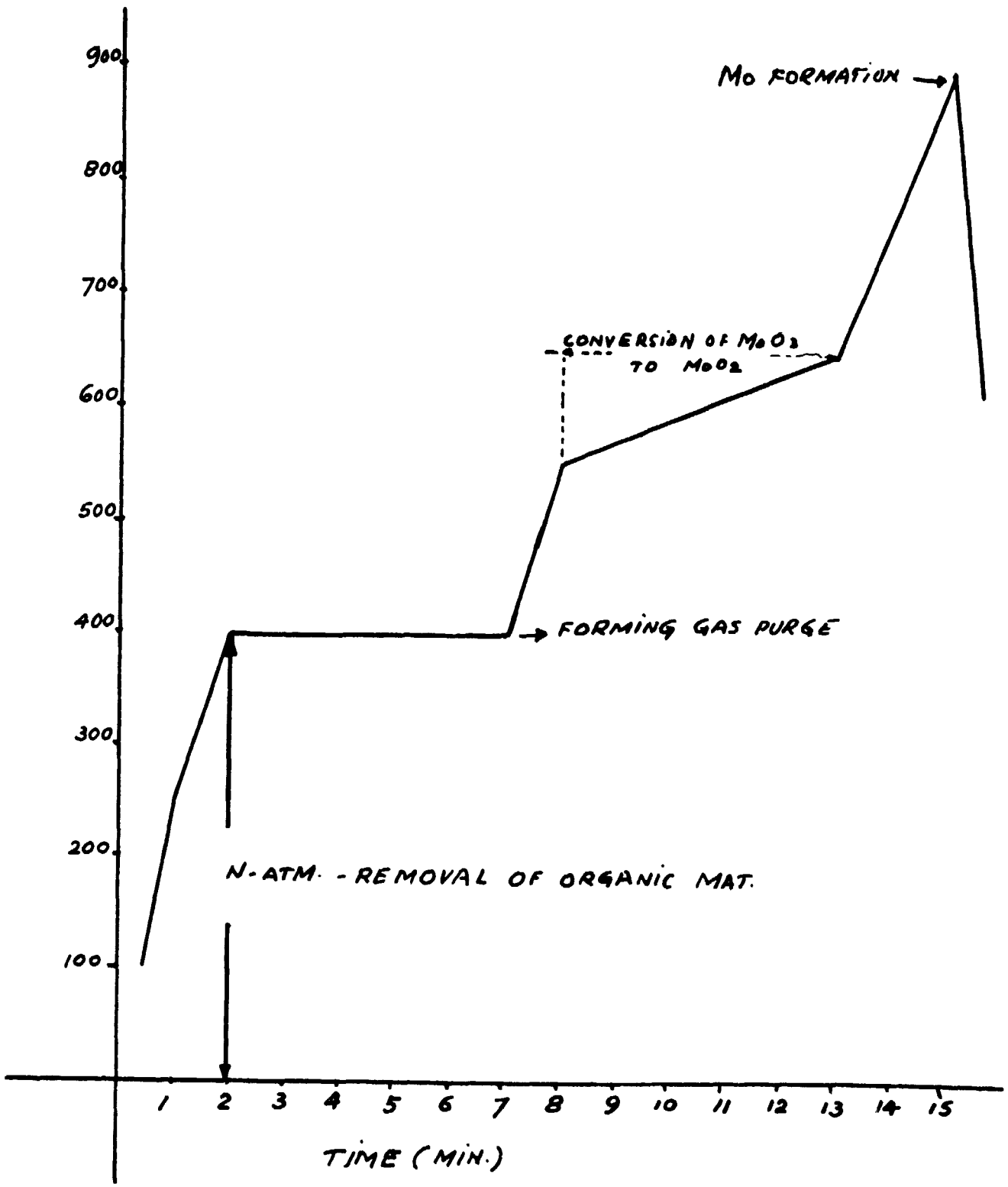
Therefore the cycle was modified to slow-down the heating rate within this range and also the peak temperature was increased to 900°C, to determine the effect of higher temperature on the bond strength.

The initial heating in nitrogen atmosphere was increased to 400°C to assure complete removal of organic materials.

A five minute purge in forming gas followed.

The graph shows the modified cycle.

CONVERSION OF MoO_3 TO Mo.
(MODIFIED CYCLE)



THE MOLYBDENUM FILM RESULTING FROM THESE CYCLES HAD LATERAL RESISTANCE BELOW 1 OHM AND COULD NOT BE SCRAPED OFF BY THE X-ACTO KNIFE.

II. 3. Determination of MoO_3:Sn ratio.

THE PRELIMINARY TESTS FOR THIS TASK WERE DONE BY COATING SILICON WAFERS WITH MOLYBDENUM OXIDE SUSPENSION AND LOCATING A FEW GRAINS OF 20 MESH SIZE TIN ON ONE EDGE OF THE COATING.

THE PURPOSE OF THIS TEST WAS TO DETERMINE THE WETABILITY OF THE MOLYBDENUM BY TIN.

THE SAMPLES WERE HEATED FOLLOWING THE MODIFIED CYCLE.

THE REACTION PROCEEDED BY FASHION PREVIOUSLY DESCRIBED FOR MoO_3. AT 900°C HOWEVER, WHEN THE Mo WAS FORMED, TIN SPREAD OVER THE ENTIRE SURFACE.

RESULTED COATINGS PASSED THE ADHESION TEST AND HAD A GOOD SOLDERABILITY BY LEAD-TIN SOLDER.

NEXT TESTS WERE DONE WITH MIXTURES OF MoO_3:Sn(325 MESH PARTICLE SIZE) USING THE FOLLOWING RATIOS.

$\frac{MoO_3}{Sn}$	$\frac{5}{5}$	$\frac{3}{7}$	$\frac{2}{8}$	$\frac{1}{9}$	$\frac{.5}{9.5}$

THE MIXTURE WAS SUSPENDED IN TRICHLORO ETHYLENE WITH ETHYLCELLULOSE BINDER SUCH AS PREVIOUSLY WITH MoO_3.

THE OBTAINED RESULTS SHOWED THAT WITH THE MoO_3:Sn RATIO GREATER THAN 3:7, THE FORMED FILMS HAD A TEXTURE WITH A LACY PATTERN WITH TIN FORMING THE RIDGES.

The bond passed the adhesion test, but the solderability was poor and required a scrubbing action.

Films formed from MoO_3:Sn ratios less than 3:7 had a dense solderable finish, but the coatings with MoO_3:Sn in ratios of 1:9 and .5:9.5 had a weaker bond.

So far the optimum seems to be at a ratio of MoO_3:Sn=2:8.

The firing cycle to achieve good bonding with this composition is between 800 and 900°C.

III. CONCLUSION

THE RESULTS FROM THE EXPERIMENTAL WORK COMPLETED IN THE FIRST QUARTER LEAD TO THE FOLLOWING CONCLUSIONS:

1. MoO_3 CAN BE CONVERTED INTO A DENSE AND ADHERENT MOLYBDENUM FILM ON SILICON WAFERS BETWEEN 800 AND 900°C.
2. THE CRITICAL PART OF THE REDUCTION PROCESS IS IN THE RANGE OF 550-650°C, WHEN MoO_3 IS REDUCED TO MoO_2. THE CONTROL IN THIS RANGE IS IMPORTANT TO PREVENT LOSSES OF MoO_3 BY SUBLIMATION.
3. MoO_3:Sn MIXTURE GIVES THE BEST RESULTS IN TERMS OF ADHESION AND SOLDERABILITY IN A RATIO OF MoO_3:Sn=2:8.

IV. PROJECTED WORK FOR NEXT QUARTER

THE WORK TO BE ACCOMPLISHED IN THE NEXT QUARTER INCLUDES THE TASKS SCHEDULED IN THE ATTACHED PROGRAM PLAN.

1. PREPARATION OF INK SAMPLES
2. SET-UP AND CALIBRATION OF TUBE FURNACE FOR FIRING THE INK ON SOLAR CELLS
3. DIFFUSION OF SILICON WAFERS FOR SCREENING OF THE INK AND FOR ELCTROLESS NICKEL PLATING TO EVALUATE THE INK ON A COMPARATIVE BASIS.

CONTRACT No: 955318

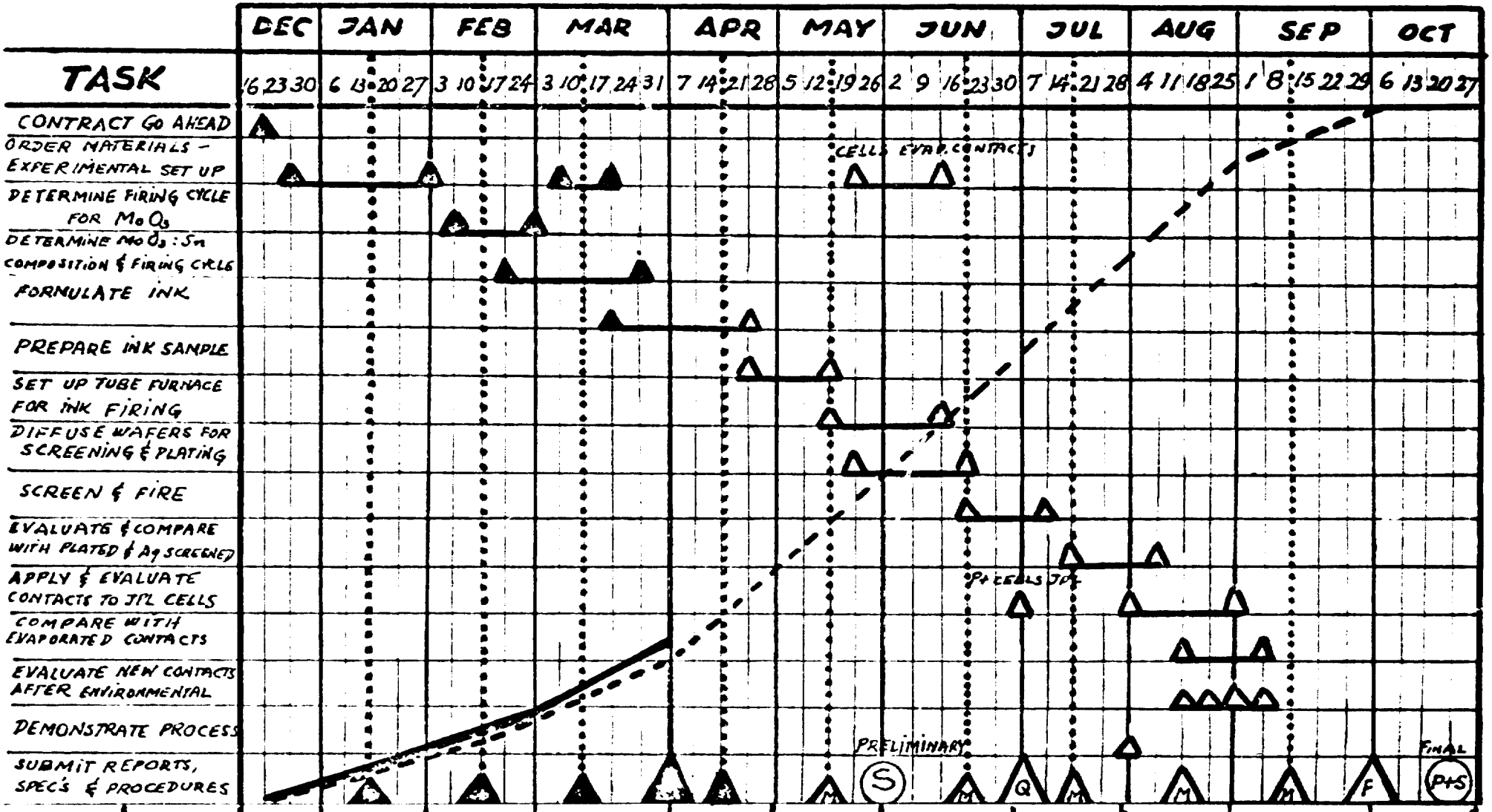
PROGRAM PLAN

FOR

A NEW METHOD OF METALLIZATION FOR SILICON SOLAR CELLS

SOL/LOS INCORPORATED
2231 S. CARMELINA AVE.
LOS ANGELES CA. 90064
(213) 820-5181

12/27/78



% COMPLETE	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT
PLANNED		5.5	14.2	23.0							
ACTUAL		6.0	15.0	25.0							

V. NEW TECHNOLOGY

NEW PROCESSES HAVE NOT BEEN SUFFICIENTLY DEVELOPED TO BE REPORTED AS NEW TECHNOLOGY. ALL NEW DEVELOPMENTS WILL BE SPECIFIED AT COMPLETION OF THE CONTRACT.